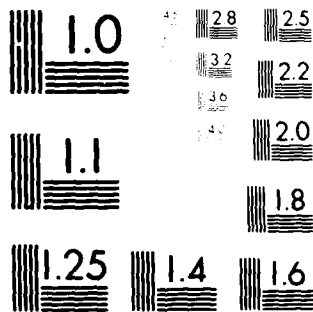


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SPECTROSCOPIC STUDIES OF THE STRUCTURE OF AMORPHOUS Se-Ge

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The Raman spectra and the average band gap of amorphous Se-Ge alloys of various compositions were measured. Both results show a discontinuous and drastic change between 45% and 50% of germanium content. The results are explained in terms of the three-fold coordinated bonds for both selenium and germanium atoms with a transfer of valence electrons from germanium to selenium atoms above 50% of germanium content.

INTRODUCTION

The bond structures of the amorphous Se-Ge alloys have been studied by infrared absorption and Raman scattering [1] [2] [3]. From these experiments, it has been conjectured that the structures of these amorphous alloys are composed of the two-fold coordinated bonds of selenium due to bonding p-electrons and the tetrahedral bonds of germanium [1] [2] [3] [4]. As the germanium content increases, linear chains or rings of selenium are bridged by the tetrahedral bonds of germanium, resulting in the increase of the melting point as well as the mechanical strength. These conjectures appear to be essentially correct from several experiments up to 33% of germanium concentration where, in the crystalline form, a hexagonal structure is accomplished with the Se-Ge bonds. However, above these concentrations of germanium, experiments are very scarce, and the appropriateness of these conjectures is quite doubtful. It is well known that the crystalline GeSe crystallizes in an orthorhombic structure based on three-fold coordinated bonds for both germanium and selenium. For the formation of three-fold bonds, valence electrons must be transferred from germanium to selenium. The excitation energy required for the transfer of valence electrons may be compensated partly by the Coulomb attraction between the ions, although the ionic bond in the amorphous state is weaker than in the crystal because of the randomness of the atomic arrangement.

We have measured the average energy gap and the Raman spectra of amorphous Se-Ge with germanium content up to 70%, and found evidence that indicates that the structure changes drastically between 45% and 50%, above which the structure is based on three-fold coordinated bonds.

PREPARATION OF SPECIMENS

Film films of amorphous Se-Ge were prepared on silica plates using evaporation technique from the ingots of Se-Ge alloys of various compositions which had been obtained by heating appropriate mixtures in an evacuated silica tube up to 1200°C. A powdered ingot was heated in a tungsten boat. To obtain the amorphous films with germanium content of less than 20% we cooled the substrate down to -20°C. By means of a simple evaporation technique, we could not get

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specimens with germanium content of more than 50%. Utilizing the flash evaporation technique, we could obtain amorphous films with germanium content from 55 up to 70%. The compositions were measured by means of X-ray micro-analysis.

AVERAGE ENERGY GAP

The average energy gap E_G of the amorphous films was obtained from the optical dielectric constant ϵ_∞ utilizing the relation [5]

$$\epsilon_\infty = 1 + (\hbar\omega_p/E_G)^2 \quad (1)$$

where ω_p is the plasma frequency for valence electrons, given by $\sqrt{4\pi Ne^2/m}$.

Here N and m are the density of valence electrons and the electron mass, respectively. The optical dielectric constant was determined from the Fabry-Perot interference patterns at $2.5\mu - 15\mu$, combined with the measured thickness of the film. The density of the valence electrons were estimated from the measured weight and the thickness of the film by assigning two electrons to each selenium atom and four electrons to each germanium atom.

The result is shown in Fig. 1. Though each data point has a rather large experimental error due to inaccuracies in the measurements in thickness and weight, it can be observed that the average gap has a maximum at 33% of germanium content and decreases sharply between 40% and 50% of germanium content. This result suggests that the structure changes completely above the 50% of germanium.

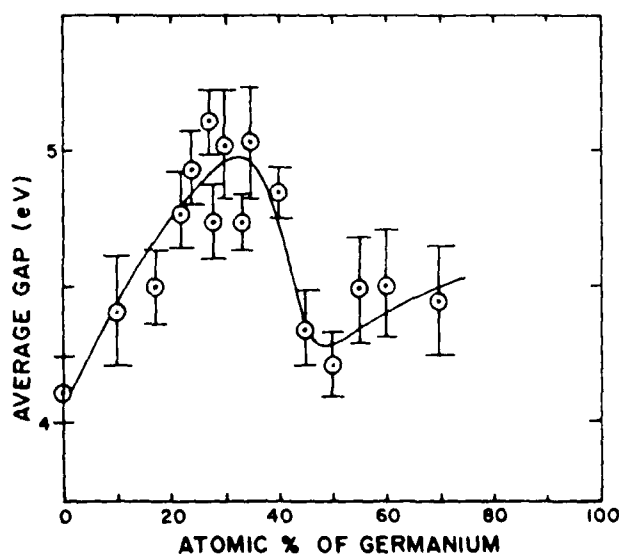


Figure 1

Average Energy Gap of Se-Ge Amorphous vs. Atomic Content of Germanium

RAMAN SCATTERING

The Raman spectra were obtained at room temperature in a backscattering configuration with He-Ne (6328 Å) and Ar-ion lasers (5145 Å) as the exciting sources. The polarization analysis was not made. To obtain the "approximate density of vibrational states," the observed Raman intensities were multiplied by a factor

$$\omega(\omega_i - \omega)^{-4} [1 - \exp(-\hbar\omega/kT)] \quad (2)$$

on the Stokes side, and a factor

$$\omega(\omega_i + \omega)^{-4} [\exp(\hbar\omega/kT) - 1] \quad (3)$$

on the anti-Stokes side under the assumption of a constant Raman tensor [9]. Here, ω and ω_i are the phonon and laser frequencies, respectively, and T is the temperature of the specimen.

The reduced Raman spectra for amorphous Se-Ge with different germanium content from 0 to 70% are shown in Fig. 2. As the germanium content increases from zero to 33%, the band at 254 - 260 cm^{-1} which is associated with the Se-Se chain bonds [4] decreases, almost disappearing at 33%, and the band peaking at 198 cm^{-1} and 216 cm^{-1} increases, giving the maximum relative intensity at 33%. This band is ascribed to the Se-Ge bonds with two-fold coordination around selenium and four-fold coordination around germanium [1] [4]. Also a broad band at 280 cm^{-1} appears with the increase of the germanium content. The intensity of this band increases further with the increase of the germanium content. This broad band may be ascribed to the tetrahedral bonds of Ge-Ge pairs [6].

Up to the germanium content of 33% our result can be well understood in terms of the chain crossing model in which the linear chain of the selenium atoms crosses at the tetrahedral bonds of germanium [4]. Above 33% up to 45% the broad band due to the Ge-Ge bonds peaking at 280 cm^{-1} increases its intensity progressively, while the intensity of the band peaking at 198 cm^{-1} and 216 cm^{-1} decreases. However, a small satellite at 182 cm^{-1} , seen in 33% and 35% samples, shoots up to a large band peaking around 175 cm^{-1} for 40% and 45% samples. The main peak at 198 cm^{-1} is associated with the breathing mode of the tetrahedral molecules of GeSe_4 in amorphous GeSe_2 , which is almost isolated from the adjacent molecules because the bond angle of selenium is about 90 degrees [7] [8]. Our conjecture is that the satellite at 182 cm^{-1} is associated with the vibrations of selenium atoms in a tetrahedral molecule in which a selenium atom is replaced by a germanium atom. The position of the satellite may shift to lower frequencies with the increase of the number of the replaced atoms. The large band at 175 cm^{-1} observed in 40% and 45% samples may be due to these vibrations.

Between 45% and 50% there is a drastic and discontinuous change in spectral pattern. The broad band at 280 cm^{-1} decreases remarkably; the band at around 175 cm^{-1} disappears, and new bands appear at 149 cm^{-1} and 96 cm^{-1} . Also the band at 198 cm^{-1} almost disappears. These changes in the spectrum suggest the disappearance of the tetrahedral molecules around the germanium atom composed of a combination of the tetrahedral bonds of germanium and the two-fold coordinated bonds of selenium.

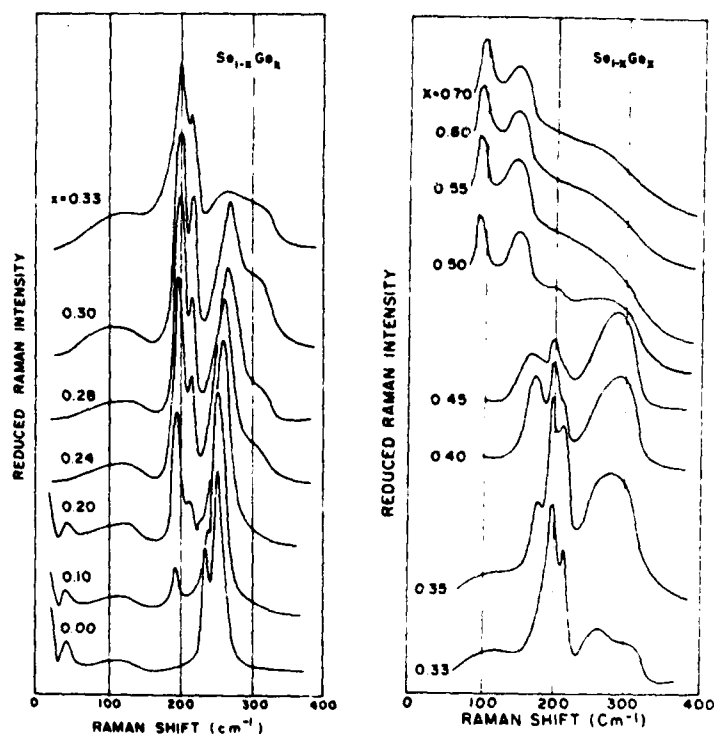


Figure 2
Reduced Raman Spectra of Amorphous Se-Ge with Atomic Content of Germanium from 0 to 70%

The spectral pattern for the 50% sample changes with heavy irradiation of the 5145 line of an argon ion laser. In Fig. 3, the change of the spectrum is shown. Spectrum A is for a virgin sample and B and C are the spectra after consecutive irradiation with the laser light of about 200 W/cm^2 for 30 minutes. It can be seen that, with irradiation, the band at 280 cm^{-1} increases; the bands at 96 cm^{-1} and 149 cm^{-1} disappear; and the bands at 175 cm^{-1} and 198 cm^{-1} appear. The new spectrum for the irradiated sample is just the continuation of the spectra for the 40% and 45% samples, indicating that the structure based on a combination of the tetrahedral bonds of germanium and the two-fold bonds of selenium is formed with the irradiation of the laser light.

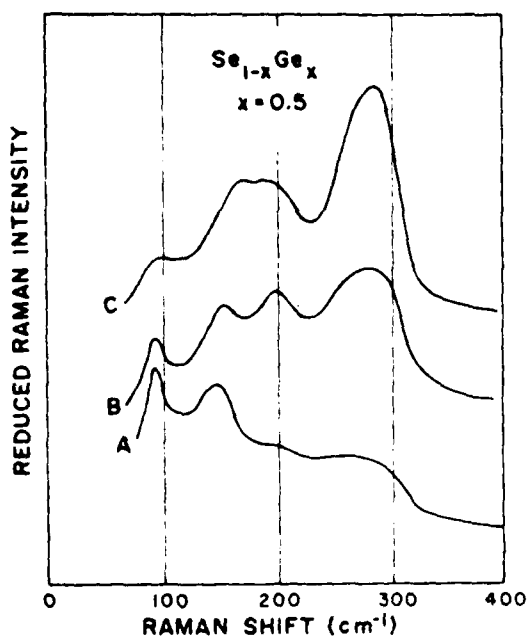


Figure 3

Raman Spectra of Amorphous Se-Ge with 50% Atomic Content of Germanium. Irradiated with 5145 Å laser light of 200 W/cm². A: Virgin Sample. B: After irradiation of 10 minutes. C: After irradiation of 30 minutes.

results, we come to the conclusion that the structure of the amorphous Se-Ge with germanium content more than 50% evaporated on a silica plate is based on the 4-2 bonds but on the 3-3 bonds. With the heavy irradiation or light, the structure is transformed into the one based on the

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